

DYNAMIC ELECTRICAL BEHAVIOR OF UNTANNED HIDE CONTAINING SORBED WATER*

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ABSTRACT

The dynamic electrical properties of untanned hide were investigated. The effect of varying the moisture content of the hide from 10% to 20% on the observed dielectric constant and loss factor was studied over the temperature range, -20° to 100°C. , and the frequency range, 50 to 100,000 cycles per second. The observed dielectric constant of the hide-water systems varied directly with temperature and inversely with frequency. This is the same type of response exhibited by many polymeric systems. The results indicate that water exhibits a typical plasticizing action on polar groups in hide substance. The data were analyzed using the theory of absolute reaction rates. Energies of activation for relaxation were calculated.



INTRODUCTION

In the development of new and improved products from hide, the mechanical properties ultimately attained are of the utmost importance. Information concerning the fundamental physical behavior of the structural units comprising raw and modified hide substance is very meager, yet it is these structural units that determine in part ultimate service performance.

In the ordinary physical test methods, a load is applied to a specimen, and the deformation produced is measured. Unfortunately, the amount of deformation observed is dependent upon the period of time that the load is applied. In other words, the mechanical properties obtained from measurement in tension, torsion, impact, etc., depend upon the rate at which the load is applied. Therefore, in order to evaluate completely a single mechanical property, it would be necessary to measure its behavior not only

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as a function of temperature but as a function of time as well. Certainly such a task would be a monumental one by conventional testing techniques. In addition, the amount of fundamental information obtainable concerning the molecular units involved in the process, and the thermodynamic and kinetic aspects of the system, are relatively limited. The data are of limited value in ascertaining the change in structure that would be desirable in modifying the properties of the system. It should be pointed out, however, that such information would be of great practical value for the engineer interested in using the material without further modification under conditions similar to those in which the specimen had been tested. It is obvious that if it were possible to make physical measurements on a material in such a way that both the fundamental physical properties and the practical behavior were obtained, we would have realized the ideal situation.

Recently a new type of test method has been used to accomplish this goal (1). In this test method the material under investigation is subjected to an alternating force, and the response of the material to this force is measured over as wide a frequency and temperature range as possible. By varying the frequency of the applied force, the time of the applied load is being varied. This method is nondestructive; that is, a single test specimen is used for the whole test and can be used to recheck any desired measurement.

The applied alternating force may either be a mechanical or an electrical one. The dynamic electrical test method was employed in the present study on untanned hide. The basic principles involved in the dynamic electrical method are contained in Debye's theory of dispersion in polar liquids (2). The molecules of a polar liquid are considered to be arranged in a relatively random fashion in the absence of an external electric field. Under the influence of a static (fixed) electric field, each molecule tends to line up (orient) with the field. The amount of alignment is a measure of the dielectric constant of the material. Upon removal of the field, a certain time is required by the molecules to return to random order. The time required for this randomization depends upon the mobility of the molecules. This time is a fundamental characteristic of the material and is called the relaxation time. If the fixed electric field is replaced with an alternating electric field, the polar molecules will follow the reversal of the field provided the frequency is low enough. Maximum motion or dielectric constant is observed. There will be no change in dielectric constant (Fig. 1) with frequency as long as there is sufficient time between reversals of the field for molecular orientation and relaxation to take place. However, as the frequency of the field is increased, a point is soon reached at which the orientation of the molecules lags behind the electric field. This lag becomes greatest when the frequency of the field is of the same order of magnitude as the relaxation (randomization) time. In addition to a decrease in dielectric constant in this range, a large consumption of energy (power) is affected by the system, which in-

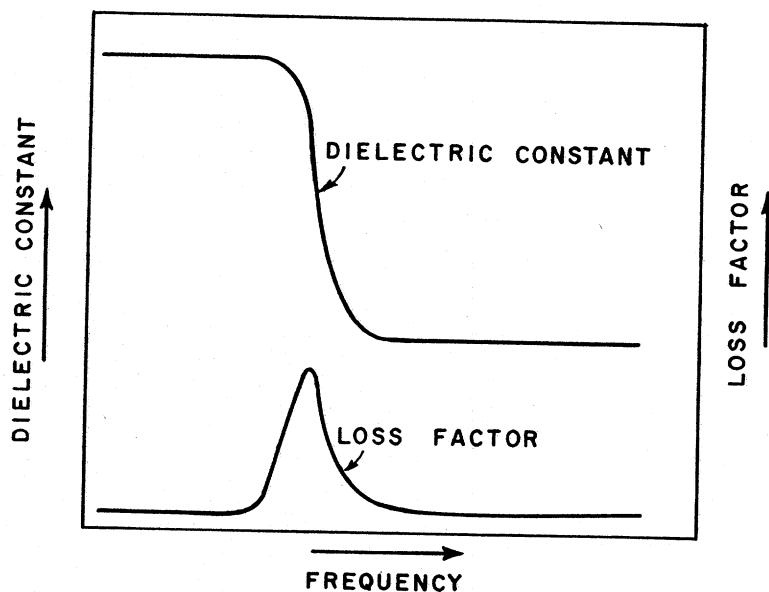


FIGURE 1.—Frequency dependence of the dielectric constant and loss factor for a polar substance.

creases with increasing frequency. This absorption of energy is generally expressed in terms of a "loss factor." It reaches a maximum value when the frequency of the applied field is equal to the molecular relaxation time. At higher frequencies the molecules have insufficient time to relax during the reversal of the field and the "loss factor" decreases until a much higher frequency is reached, at which time both the "dielectric constant" and "loss factor" are at a minimum and do not change further with increase in frequency.

It might be asked why the molecules are unable to follow the electric field at the higher frequencies. It was stated previously that the ability of the molecule to orient in the field depended upon the mobility of the molecules or the viscosity of the medium. Therefore, at the higher frequencies, the viscosity is too great for orientation of a molecule within the short time of each cycle. It is well known that viscosity varies with the temperature. Thus it is possible, simply by increasing the temperature, to increase the number of molecules that have sufficient energy to overcome intermolecular interactions and would therefore be able to follow the electric field. Thus, one feature of dynamic measurements is that time (frequency) and temperature can be interchanged (1).

Numerous investigations into the dynamic electrical properties of polar polymeric materials have shown that they exhibit a behavior similar to that

of the polar liquids. Fuoss (3) investigated polyvinyl chloride polymers containing various amounts of diphenyl as a plasticizer. Würstlin (4) studied the efficiency of plasticizers in polymer molecules. Müller (5) has discussed the theory of relaxation in rubbery materials relative to dielectric behavior. Flow processes in polymeric systems have been considered relative to dielectric properties by Scheele and Timm (6). In a recent article, de Brouckere and Offergeld (7) reported the influence of different molecular parameters on the dielectric characteristics of a number of macromolecules. Many other investigations have been made along similar lines on a wide variety of natural and synthetic macromolecular systems. All studies yielded information of a fundamental nature about the ultimate molecular behavior of the particular substance studied. It should be pointed out that only small portions of the macromolecular chain undergo orientation in an electric field, in particular only those portions containing polar groups.

In view of the wide application of the dynamic electrical test method to other macromolecular systems, a search of the literature was undertaken to determine the extent of its application to hide and leather substances. This search revealed that only a few studies (8, 9, 10) had been made. Therefore, an investigation was initiated to ascertain the suitability of hide substance for such studies and to determine if basic information could be derived from the data obtained. Untanned hide was selected for the initial study because it is the simplest hide system. The results would not be complicated by any modifying affects that tanning agents, fatliquors, etc., might introduce.

This communication describes the dielectric behavior of untanned hide as a function of time (frequency of applied force) and temperature. In particular, the influence of sorbed water vapor on the dynamic electrical properties was investigated.

EXPERIMENTAL

Specimens.—The hide used in the experiments was pickled cowhide grain splits and pickled calfskins obtained from tanneries. They were subsequently depickled with sodium acetate to pH 4.9, washed in running tap water, and dehydrated in acetone. Disc-shaped specimens, cut from hide, were 1.75 inches in diameter and up to .150 inches thick. The specimens were dried under vacuum at 50° C. to constant weight. The dried specimens were equilibrated in a vacuum desiccator in a water vapor atmosphere for various periods of time depending upon the water content desired. Upon removal from the desiccator and subsequent weighing, the specimen was sealed in a double layer of polyethylene film, thickness 0.001 inch, to prevent loss of water during the electrical measurement. The hide sample plus its polyethylene covering was weighed before and after each investigation.

Before electrical measurements were undertaken, the specimen was conditioned at the maximum temperature to be employed for the specific hide-water composition being studied. The maximum temperature at which measurements were made was at least 10° below the apparent melting (shrinkage) temperature of the system (11).

Apparatus.—The electrical properties were determined with a General Radio Company* capacitance-measuring assembly containing the following components: Type 716-C capacitance bridge, Type 1302-A oscillator, Type 1474 amplifier and null detector equipped with Type 1603-A filter, and Type 1690 dielectric sample holder. The temperature of the specimen was assumed to be that registered by a thermocouple inserted in the sample holder. The temperature in the range -20° to 100° C. was maintained to $\pm 0.5^{\circ}$ C. by circulating air from a constant-temperature bath through the sample holder which had been insulated. Constant readings were not obtainable until equilibrium had been established throughout the sample. Measurements generally were made at 5° or 10° intervals through the range and at 50, 100, 1000, 3000, 10,000, 30,000, and 100,000 cycles per second. Other temperature and frequency intervals were selected in those regions where rapid changes in the electrical behavior of the system were observed.

RESULTS

Untanned hide-water system.—Figure 2 shows the variation in the observed dielectric constant, ϵ' , with frequency for a specimen of untanned acetone-dehydrated hide containing 20% water. The observed dielectric constant at each of the temperatures investigated (-20° to 60° C.) decreases with increasing frequency. The corresponding variation in the observed loss factor, ϵ'' , for this system is shown in Fig. 3. The loss factor curves obtained at 20° , 40° , and 60° C. show the presence of a maximum. The frequency range employed was not broad enough to show these maxima at 0° and -20° C. Only a fraction of the data collected are presented in the figures.

Untanned hide specimens taken from different sections of the same hide as well as other hides qualitatively yield similar-shaped dielectric and loss factor curves. Both calfskins and cowhides were investigated. Although the region in which dispersion occurred was about the same for all specimens, the magnitudes of the observed dielectric constant and loss factor were quite variable. However, this does not affect the results reported herein, as only the relative changes in the observed data were employed in the treatment of the data.

*Mention of commercial products does not constitute an endorsement of such to the possible detriment of other products not mentioned.

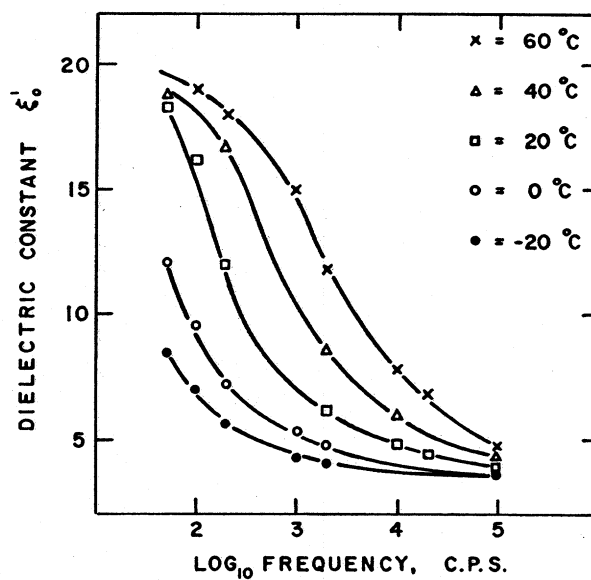


FIGURE 2.—Frequency dependence of the observed dielectric constant for untanned hide containing 20% water.

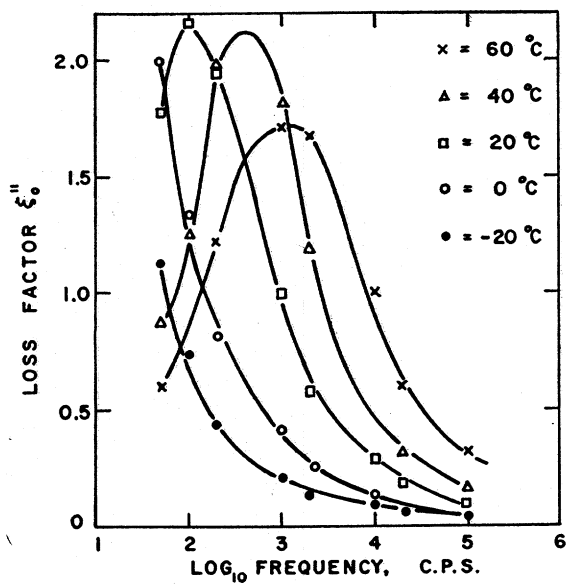


FIGURE 3.—Frequency dependence of the observed loss factor for untanned hide containing 20% water.

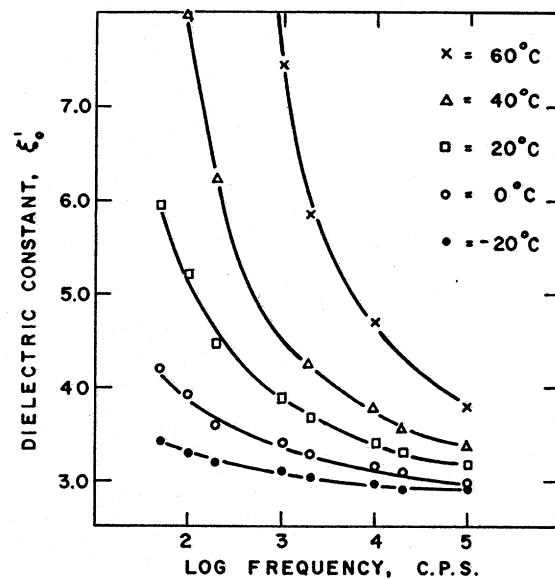


FIGURE 4.—Frequency dependence of the observed dielectric constant for untanned hide containing 16% water.

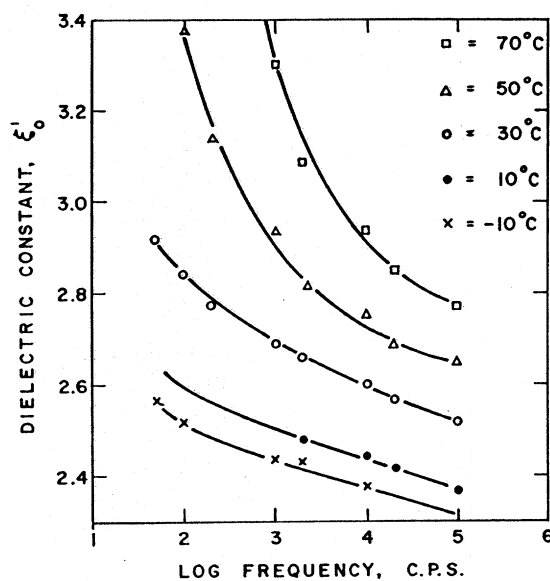


FIGURE 5.—Frequency dependence of the observed dielectric constant for untanned hide containing 10% water.

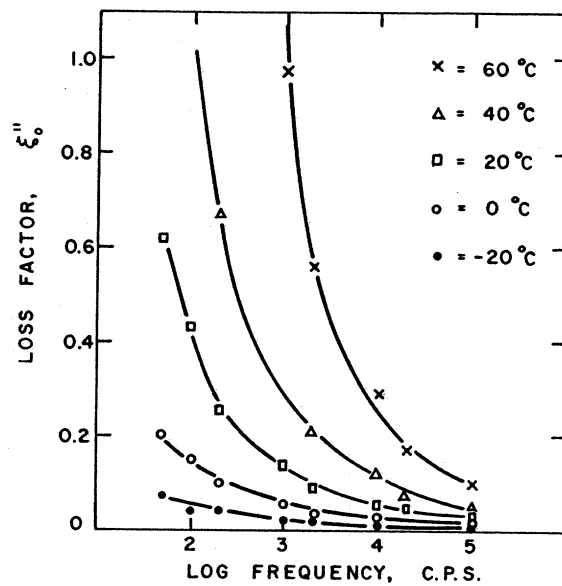


FIGURE 6.—Frequency dependence of the observed loss factor for untanned hide containing 16% water.

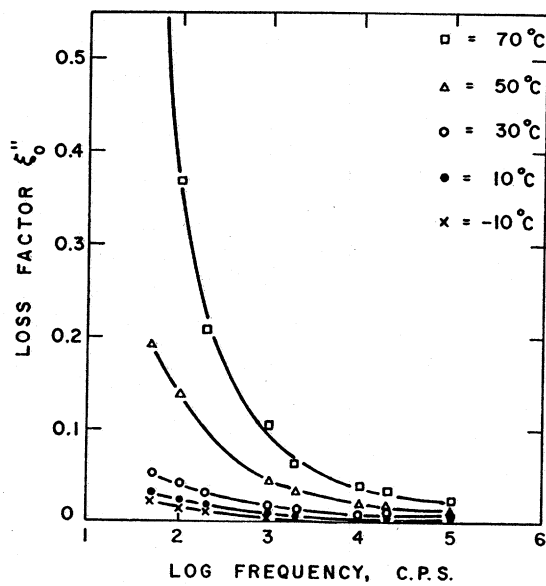


FIGURE 7.—Frequency dependence of the observed loss factor for untanned hide containing 10% water.

Variation in electrical behavior with water content.—Figures 4 and 5 show the variation in the observed dielectric constant, ϵ'' , and Figs. 6 and 7 show the variation in observed loss factor, ϵ'' , with frequency in the temperature range -20° to 60° C. for the specimens of untanned hide containing 16% and 10% of water. In both cases the observed dielectric constant decreases with increase in frequency. A much smaller portion of the curve was attainable in these cases because of the frequency and temperature limitations. This is quite apparent from an examination of the observed loss factor data. Loss factor maxima were not attainable for untanned hide substance under the conditions employed below about 20% moisture content.

DISCUSSION

Effect of temperature and moisture content on dipole rotation.—The general shapes of the frequency dispersion curves (Figs. 2, 4, 5) and the loss factor curves (Figs. 3, 6, 7) demonstrate that the hide-water systems investigated show dielectric relaxation. It is argued that this is due to dipole reorientation. Both the dielectric constant and loss factor curves are shifted along the frequency scale by temperature. As the temperature is increased the number of dipoles possessing sufficient energy for overcoming the barriers opposing liberation is increased. This behavior is similar to that exhibited by many polymeric systems (3, 12, 13, 14, 15). Similarly, the dielectric constant and loss factor curves are shifted along the frequency scale by the amount of sorbed water present in the hide specimen. As the amount of sorbed water is increased the number of dipoles moving in the field is increased.

One possible explanation for this observed behavior is that the water molecules might be acting as a plasticizer. Water molecules could be considered as solvating accessible polar groups of the protein molecules that comprise the hide system. In forming hydrogen bonds with the polar groups, interchain bonding would be expected to decrease. These free polar groups would now be available for orientation in an electric field. The larger the number of water molecules present, the greater the number of freed polar groups. After all polar groups were solvated, additional water should have little effect on the system. Under the proper condition a measure of the available polar sites along the chains might be attainable.

Recently, Boyd (16) studied the dynamic electrical behavior of polyhexamethylene adipamide. It was demonstrated that water molecules are attached so strongly to this polymer chain through hydrogen bonding at amide groups that the water molecules move the chains as they change configuration and hence increase the dipole moment of the amide groups. A similar situation would be expected to exist in the present study.

It has been shown (17) that dielectric data can be interpreted by utilizing the theory of absolute reaction rates. The frequency, f , at which the loss factor, ϵ'' , at a given temperature is at a maximum, was used to define a temperature-dependent dielectric relaxation time, τ . Examination of the loss factor data shows that with increasing amounts of water the loss maximum shift to higher frequencies at the same temperature. In other words, the time for dipole relaxation is decreased, illustrating the plasticizing action of the sorbed water.

The relaxation time can be obtained from the frequency of maximum loss by the relationship

$$\tau = 1/(2\pi f_{\max})$$

Application of the theory of absolute reaction rates (16) yielded the following expression:

$$1/\tau = 2\pi f_{\max} = (kT/h)e^{\Delta S^\ddagger/R} e^{\Delta H^\ddagger/RT}$$

where k is Boltzmann's constant, h is Planck's constant, T is absolute temperature, R is gas law constant, and ΔS^\ddagger and ΔH^\ddagger are the entropy and energy of activation, respectively. Figure 8 shows the plot of the relaxation time ($\log 2\pi f_{\max}$) vs. $1/T$ for untanned hide containing 20% water. The data form a straight line in the temperature range employed. The energy of activation for relaxation, ΔH^\ddagger , calculated from the slope of the linear plot, was 21 kcal/mole.

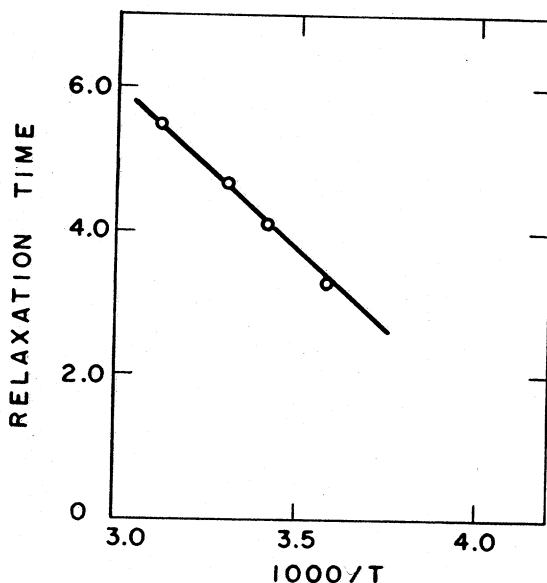


FIGURE 8.—Variation of the maximum loss factor (relaxation time) with reciprocal absolute temperature for hide containing 20% water.

Equivalence of frequency and temperature in hide-water systems.—Ferry and coworkers (18, 19, 20) developed a method for transforming the temperature and frequency scales so that the observed values obtained from electrical or mechanical measurements can be brought on to a single master curve. This is accomplished by first reducing the observed dielectric constant, ϵ'_o , and loss factor, ϵ''_o , values to the same reference temperature by means of the following expressions:

$$\epsilon'_r = \epsilon'_o \left[\frac{T}{T_o} + \left(\frac{\epsilon'_\infty}{\epsilon'_o} \right) \left(1 - \frac{T}{T_o} \right) \right]$$

$$\epsilon''_r = \epsilon''_o \left(\frac{T}{T_o} \right)$$

where ϵ'_r is the reduced observed dielectric constant, ϵ'_o is the observed dielectric constant, T is the absolute temperature at which measurements were made, T_o is an arbitrarily selected reference temperature (300° A. is used herein), ϵ'_∞ is the limiting value of ϵ'_o at high frequency and low temperature, ϵ''_r is the reduced observed loss factor, and ϵ''_o is the observed loss factor. (No corrections were employed for any density changes.)

The log of the reduced electrical data obtained at each temperature is plotted against the log of the angular frequency ($\omega = 2\pi f$) on separate transparent sheets of graph paper. The curves for the various temperatures are then superimposed by a linear shift along the log frequency axis. If frequency and temperature are equivalent, the transformed observations of the same kind will fall on a continuous or "master" curve. Application of the method of reduced variable to the dielectric data obtained on the hide specimen containing 20% moisture resulted in the two master curves shown in Fig. 9. Apparently in this hide-water system all the electrical relaxation times have the same temperature dependence.

From the amount of displacement on the log frequency axis required to superimpose the reduced data at the various temperatures, a factor b_T can be obtained (18, 19, 20). The factor b_T has been defined as the ratio of the dielectric relaxation time at temperature T to that of the reference temperature, T_o . A plot of $\log b_T$ against $1/T$ permits the apparent activation energy for dielectric relaxation, ΔH^\ddagger , to be calculated over the temperature range employed. In Fig. 10 the plot $\log b_T$ vs. $1/T$ is essentially linear over the temperature range employed, -20° to 60° C. for the hide specimen containing 20% moisture. Its ΔH^\ddagger value is 21 kcal/mole, which is identical with the value obtained from the maxima in loss curves previously discussed. The advantage of this latter method for treating the dielectric data is that energies of activation can be obtained from a limited amount of data at a

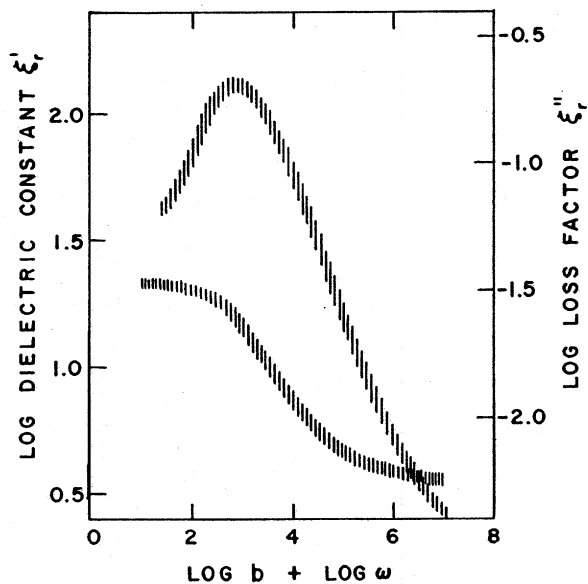


FIGURE 9.—Variation of reduced dielectric constant and loss factor with reduced frequency for hide containing 20% water (master curve).

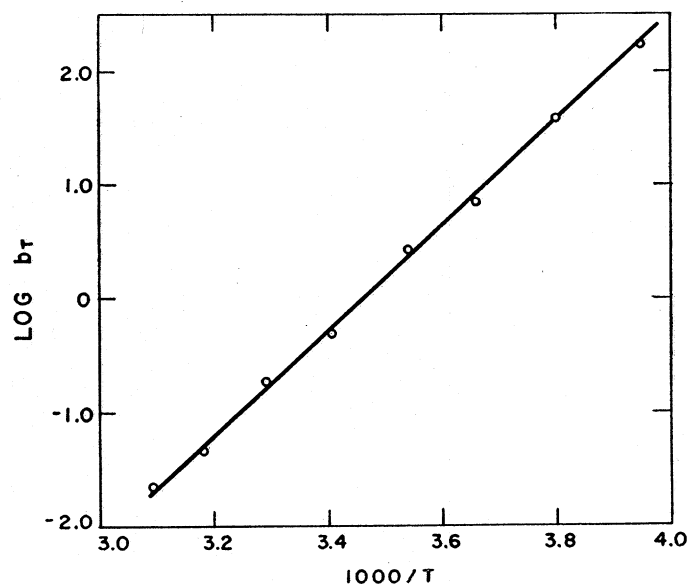


FIGURE 10.—Variation on the frequency reduction factor, bT , with reciprocal absolute temperature for hide containing 20% water.

few temperatures from either the observed dielectric data or the loss factor data. No maxima are required in this treatment. Therefore, it was possible to obtain energies of activation of dipole orientation for untanned hide containing 16% and 10% sorbed water. The corresponding values are given in Table I. The apparent energy of activation was within the limits of

TABLE I
APPARENT ENERGY OF ACTIVATION FOR RELAXATION IN UNTANNED
HIDE AS A FUNCTION OF WATER CONTENT

Percent Water	ΔH^\ddagger , Kcal/Mole
20	21
16	20
10	21

experimental error, the same for untanned hide containing between 10% and 20% sorbed water. This would indicate that the type of dipoles undergoing reorientation is the same, while the number participating is increasing with increase in water content.

A number of hide-water specimens were investigated without the polyethylene cover. To reduce the loss of water to a minimum, electrical measurements were restricted to the temperature range -40° to 20° C. In the 10% to 20% moisture range the relative electrical behavior of the hide specimen was identical to that obtained with the polyethylene-covered hide system. Superposition of the observed dielectric data gave apparent energies of activation that were also in very good agreement.

It has been suggested from the data obtained that some polar groups of untanned hide are able to respond to an electric field when the system contains between 10% and 20% sorbed water. It is well known that the physical properties of a substance depend upon the response of its structural components at the molecular level to a mechanical load. If the sorbed water in the concentration range studied is acting as a plasticizing agent for hide, then its mechanical response should also change. Torsional modulus measurements on three different untanned hide specimens showed a small, about 15%, but definite decrease in modulus when the moisture content of the hide specimen was increased from 10% to 20%.

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